Structure and bonding in phosphide clathrate thermoelectrics

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The phenomenon of thermoelectricity is attributed to the interconversion of thermal and electrical forms of energy. We developed a new class of bulk thermoelectric materials based on clathrates with a three-dimensional framework comprised of oversized transition metal-phosphorus polyhedral cages that encapsulate guest cations [1-8]. Transition metal-based clathrates exhibit high thermal and chemical stability, a large variety of framework topologies, and a high tunability of the electronic properties via framework substitutions. Chemical bonding in the clathrate framework between two drastically different element types, phosphorus and late transition metals, caused different versions of the complex long- and/or short-range orderings as was revealed by a combination of synchrotron and neutron diffractions and pair distribution function analyses, scanning-transmission electron microscopy, and ^{31}P solid state NMR. The correlation between the crystal structure, distribution of the metal and phosphorus atoms over the clathrate framework and thermoelectric properties will be discussed.

1. Wang, J.; He, Y.; Mordvinova, N. E.; Lebedev, O. I.; Kovnir, K. *Chem,* **2018,** *DOI: https://doi.org/10.1016/j.chempr.2018.04.001*.
2. Wang, J.; Dolyniuk, J.; Kovnir, K. *Acc. Chem. Res.* **2018,** *51,* 31.
3. Dolyniuk, J.; Wang. J.; Marple, M.; Sen, S.; Cheng, Y.; Ramirez-Cuesta, A. J.; Kovnir, K. *Chem. Mater.* **2018,** *DOI: 10.1021/acs.chemmater.8b00966*.
4. Wang, J.; Wang, L.-L.; Kovnir, K. *J. Mater. Chem. A* **2018,** *6,* 4759.
5. Dolyniuk, J.; Zaikina, J.V.; Kaseman, D.C.; Sen, S.; Kovnir, K. *Angew. Chem. Int. Ed.* **2017,** *56,* 2418.
6. Wang, J.; Lebedev, O.I.; Lee, K.; Dolyniuk, J.; Klavins, P.; Bux, S.; Kovnir, K. *Chem. Sci.* **2017,** *8,* 8030.
7. Dolyniuk, J.; Whitfield, P.S.; Lee, K.; Lebedev, O.I.; Kovnir, K. *Chem. Sci.* **2017,** *8,* 3650-3659.
8. Dolyniuk, J.; Owens-Baird, B.; Wang, J.; Zaikina, J.V.; Kovnir, K. *Mater. Sci. & Engin. R.* **2016,** *108,* 1.

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